Materials for Multiphoton 3D Microfabrication

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Abstract

Two-photon/multiphoton lithography (MPL) has emerged as a versatile technique for the fabrication of complex 3D polymeric, hybrid organic/inorganic, and metallic structures. This article reviews some recent advances in the development of molecules and materials that enable two-photon and multiphoton 3D micro- and nanofabrication. Materials that exhibit high sensitivity for the generation of reactive intermediates are described, as are various materials systems that enable functional devices to be made and in some cases enable structures to be replicated. The combination of advances illustrates the opportunities for MPL to have a significant impact in the areas of photonics, microelectromechanical systems, and biomedical technologies.

Introduction

There is a growing interest in the fabrication of truly three-dimensional microstructures and devices for potential applications in photonics, microelectromechanical systems, microfluidics, and tissue engineering, among other fields.[1–3] In 2D lithography, major advances have been made in decreasing the feature sizes in devices. For example, lithographic processes for making complex integrated circuits with 65-nm features are now used in the commercial production of microprocessors,[4] but these processes are restricted to 2D patterning in a given exposure step. Progress also has been made in using molecular, nanotube, and nanoparticle self-assembly to build structures with unique properties in a bottom-up approach.[5–7] Such self-assembly processes, however, are limited predominantly to the formation of periodic structures. Fabrication of 3D objects of arbitrary shapes with feature sizes approaching those achievable by either photon or electron-beam lithography traditionally has been an extremely difficult task. Some types of 3D structures can be fabricated using sequential layer-by-layer lithographic processes,[8] direct-writing with inks,[9] stereolithography,[10] and multibeam interference lithography,[11] which have limitations in terms of being quite restricted in the range or the spatial resolution of 3D structures that can be formed, or are consuming in terms of the number of masks and amounts of solvent required. Many new or emerging technologies demand fabrication of 3D structures with submicron feature sizes and great flexibility in shape and material composition. Two-photon/multiphoton lithography (MPL) offers the potential for micro- and nanofabrication of arbitrary 3D structures in a single coat/expose/develop process cycle. In this article, we review the development of two-photon absorbing materials that can be used for 3D microfabrication of a variety of complex structures.

Two-Photon/Multiphoton Lithography

Two-photon absorption (2PA) provides a means of activating chemical or physical processes with high spatial resolution in three dimensions and feature widths as small as ~100 nm. With sufficiently intense light, such as from a pulsed laser beam, it is possible for a molecule to simultaneously absorb two photons, each approximately half the energy (twice the wavelength λ) normally required to reach an excited state. The 2PA process is weak relative to one-photon excitation for intensities below about 10 GW/cm^2 and nominal values for the absorption cross sections. The probability of a molecule absorbing one photon is proportional to the intensity of the excitation beam. In contrast, the probability of a molecule absorbing two photons simultaneously is proportional to the square of the intensity of the excitation beam.

The nonlinear intensity dependence of 2PA gives rise to some very interesting and useful effects. First, 2PA enables the excitation of molecules with a very high degree of spatial confinement in three dimensions,[12] leading to feature widths of ~100 nm and excited volumes as small as ~0.003 μm^3 or 3 attoliters. This 3D control of the excitation arises from focusing an intense laser beam into a material and the fact that the beam intensity decreases roughly quadratically with the distance from the focal plane. Because the probability of 2PA is proportional to the square of intensity of the laser beam, the probability of 2PA falls off roughly as the fourth power of the distance from the focus. Consequently, 2PA at appreciable distances from the focal plane (say, at roughly twice the Rayleigh length, or 2.5 times the beam radius at the focus) is negligible (5%), relative to that at the focal plane, leading to a much greater confinement of excitation along the direction of propagation and at the focus of the beam for 2PA as compared with one-photon absorption (Figure 1a). Second, with 2PA it is possible to excite molecules at increased depth, relative to one-photon absorption, in a nominally high-absorbing medium, because the photon energy lies well below that at which the medium absorbs via one-photon absorption (Figure 1b). With these features of higher resolution and the ability to "write" at different depths, 2PA has enabled the realization of 3D optical data storage,[13–16] lithographic microfabrication,[15,17] and imaging[12] via pulsed laser excitation. By computer-controlled scanning of the focus of a laser beam within a photochemically active precursor material, many complex 3D structures can be fabricated with submicron resolution (see Figure 1c for a schematic illustrations of an MPL system).

MPL is helping to revolutionize the fabrication of 3D structures on the submicron scale, because of the following advantages:

1. The numerous types of 3D structures that can be fabricated, including ones with interlocking or movable parts;
2. The ability to directly pattern various materials ranging from transparent

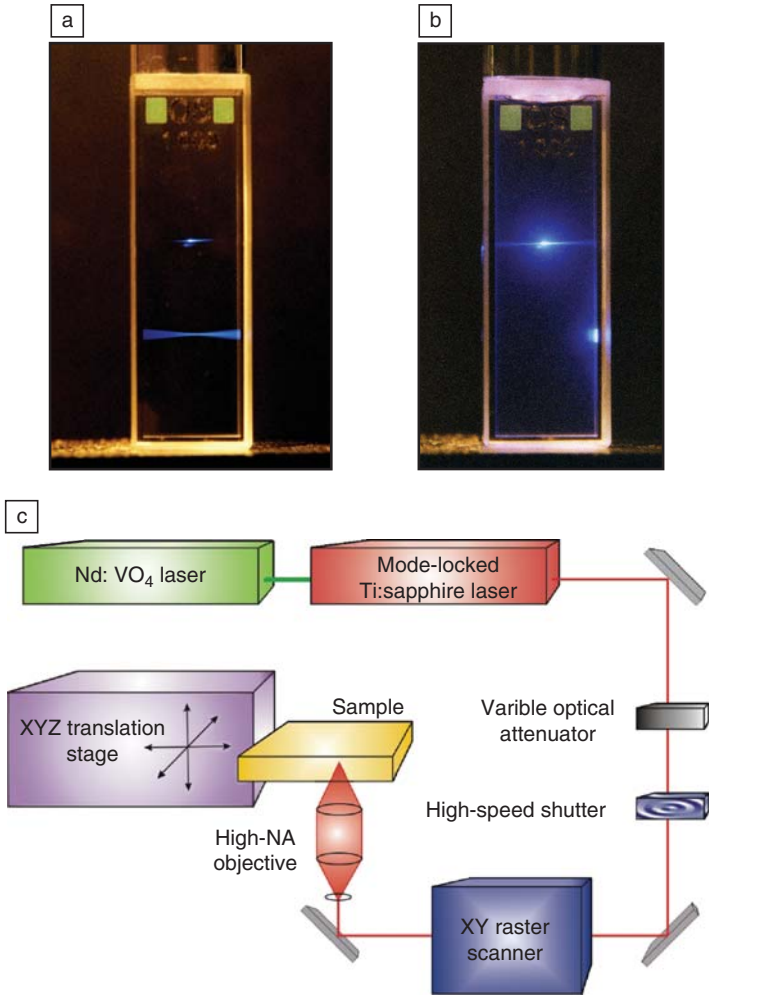

Figure 1. (a) Fluorescence/optical image demonstrating localized excitation in three dimensions by two-photon excitation. Top spot, two-photon excitation; bottom streak, one photon excitation. (b) Demonstration of the limited penetration depth of one-photon excitation in a strongly absorbing medium (bottom spot at right edge of cuvette); improved penetration depth via two-photon excitation is clearly seen by the intense spot in the central upper portion of the cuvette. (c) Schematic illustration of a system for two-photon/multiphoton 3D microfabrication.

polymers to inorganic–organic hybrids to metals;
3. The possibility to create "micromolds" that can be used for templated growth of a range of materials, enabling the integration of disparate materials into devices;
4. The capability to fabricate features from the nanoscale (<100 nm) to the microscale, providing a technology for integrating nanostructures with well-established microscale components.

Thus, two-photon/multiphoton 3D lithography is a disruptive technology that fundamentally changes what 3D microstructures can be fabricated and how they can be made.

Two-Photon Absorption Materials and Processes

To exploit these advantages, it is beneficial to use specially designed and engineered photoactive materials within which it is possible to localize photochemical reactions within the excitation volume. Whereas various efforts to exploit 2PA in 3D microfabrication and imaging have been reported, many of these schemes have employed conventional photoinitiators or fluorescent chromophores that were developed for use under one-photon excitation conditions. Such chromophores typically had low efficiency for 2PA (characterized by the 2PA cross section, δ).[18] Accordingly, schemes that seek to exploit the use of 2PA would be aided by the development of molecules with large δ. One key to the design of molecules with high sensitivity in 2PA is a detailed understanding of how δ depends on molecular structure. Molecules with a large δ would be more efficiently excited than molecules with a small δ at the same laser intensity, enabling the use of lower-power and less costly pulsed lasers[19] and increasing the speed with which scanning laser exposures could be made, thus making 2PA applications more economically feasible. Recent advances in two-photon materials and processing methods suggest the promise for MPL to become a mainstream, commercially viable fabrication technology, as we briefly describe here.

Before 1998, the largest value of δ reported was roughly 300 GM for the laser dye rhodamine B (where 1 GM ≡ 1×10^{-50} cm^4 s).[20] We discovered that *E*-4,4′-bis(di-*n*-butyl)aminostilbene, **1**, had a peak two-photon excitation cross section δ_{max} = 210 GM at 605 nm, which is almost 20 times greater than the peak cross section for *trans*-stilbene.[21] The δ value for **1** was among the largest values of δ reported for organic compounds at that time. Quantum-chemical calculations were performed to gain insight into the much larger δ_{max} value for **1** compared with *trans*-stilbene. The 2PA spectra were obtained from the dispersion of the imaginary part of the second hyperpolarizability using the sum-over-states expression from perturbation theory that reproduced the experimentally observed order-of-magnitude enhancement in δ_{max} upon substitution of *trans*-stilbene with terminal dialkylamino groups. The calculations showed that the lowest singlet excited state (e) is a one-photon-allowed state with B_u symmetry, whereas the second singlet excited state (e′) is two-photon-allowed with A_g symmetry and corresponds to the observed 2PA peak. The calculations also suggested that the ground-state to excited-state (g → e) excitation is accompanied by a substantial charge transfer from the amino groups to the central vinylene group, leading to a large change in quadrupole moment upon excitation; a similar sense and magnitude of charge transfer is calculated for the g → e′ transition. This pronounced redistribution of the π-electronic density was correlated with a significant increase in the e→e′ transition dipole moment, which is the major contributor to the enhanced two-photon cross section of **1** with respect to that of *trans*-stilbene. Because the symmetric charge transfer and change in quadrupole moment appeared to be corre-

lated to the increase of the two-photon cross section, we examined systems in which the π-conjugation length between the two-donor groups (*D*-π-*D* chromophores) was increased and in which acceptor groups were attached to the center of the π-conjugated bridge (*D*-*A*-*D* chromophores), and similarly in which the sense of the symmetric charge transfer was reversed (*A*-π-*A* and *A*-*D*-*A* chromophores).[21] In this manner, many compounds that exhibited large δ were identified. Some of these compounds were strong excited-state–reducing agents and were used for MPL, as described next.

Two-Photon Initiated Chemistry for 3D Microfabrication

Several groups have used the capabilities of 2PA to demonstrate 3D optical data storage and MPL using various photoactivated reactions (such as photoinitiated polymerization and fabrication of hybrid materials,[15,17,22–25] photocleavage of functional groups,[26,27] photoreduction of metals,[28–30] and photochromic reactions[31,32]). We have developed highly efficient two-photon photopolymer resins based on our high-δ chromophores that exhibit a photosensitivity increase of 20- to 50-fold relative to photopolymer resins incorporating photoinitiators designed for one-photon lithography.[15] In the MPL scheme employed, two-photon excitation of a *D*-π-*D* chromophore initiates free-radical cross-linking in a multifunctional methacrylate photopolymer blend that reduces the solubility of the exposed material. In this process, an arbitrary 3D pattern is impressed into the photopolymer by scanning the focus of an intense laser beam within the material (see Figure 2a). The exposed 3D pattern can then be developed by dissolving the unexposed material with a suitable solvent to give a freestanding 3D microstructure in a single exposure/development cycle.

The MPL approach can be used to produce a variety of interesting 3D microstructures including integrated optical elements[1,15,33] as well as micromechanical and complex interlocking structures,[34,35] such as the freestanding microchain shown in Figure 2b.[36] Three-dimensional periodic structures are currently of interest as photonic crystals, which have unique optical reflection/transmission and dispersion properties.[15,36–40] Figure 3a shows a view of a 3D periodic "stack-of-logs" structure that has an in-plane rod spacing of 4 μm and a layer spacing of 1.5 μm, as appropriate for diffraction of infrared radiation.

The 20- to 50-fold increase in two-photon photosensitivity, relative to conventional initiators, discussed earlier for

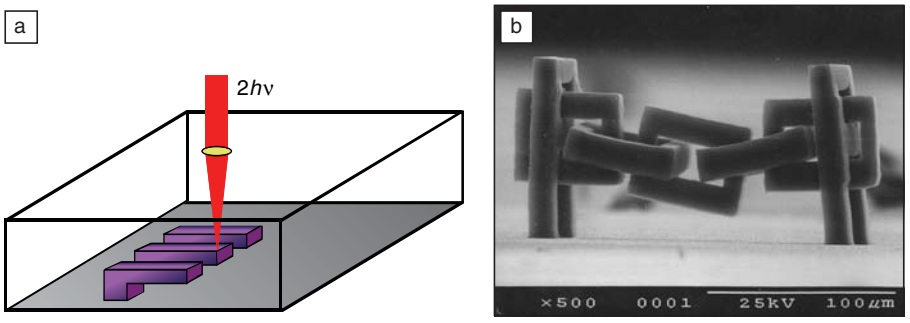

Figure 2. (a) Schematic illustration of scanning laser exposure of a two-photon absorbing photopolymer resin in multiphoton lithography (MPL). (b) Freestanding microchain fabricated by MPL; the entire structure is approximately 150 μm from end to end.

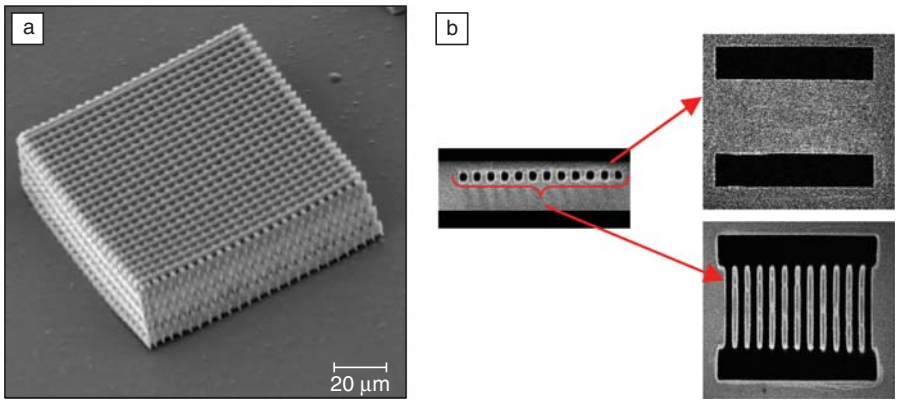

Figure 3. (a) Polymeric "stack-of-logs" photonic crystal structure fabricated using MPL; the width of the whole structure is comparable to that of a human hair. (b) Cross-sectional views of a tunnel array structure fabricated by MPL using a chemically amplified positive tone resist and a high-sensitivity two-photon photoacid generator. The upper right image is a top view showing the vertical channels that open to the surface. Each tunnel in the structure is 4 μm wide.

D-π-*D* dyes was due almost entirely to their large δ. We estimated that several of these two-photon initiators exhibit only modest radical generation efficiencies after excitation ($\Phi_R \sim 0.03$, where Φ_R is the quantum yield for radical generation from the excited state). Because the overall photosensitivity for a two-photon photoactivator is dependent on $\delta\Phi_c$ (with Φ_c being the quantum yield for generating a reactive species), these results indicated that significant further improvements in photosensitivity were possible. Thus, a key challenge in developing efficient two-photon photoactivators was the requirement that the molecule or molecular ensemble simultaneously have a large two-photon cross section and an efficient excited-state pathway to activate a reaction.

These requirements put restrictions on the energy and lifetime of the relaxed excited state formed after two-photon excitation. Many conventional photoactivator systems, including radical photoinitiators, photoacid generators, and photodeprotection systems, involve excitation of ultraviolet-absorbing chromophores that directly leads to bond cleavage. Photodeprotection is the process of masking a functional group (for example, an amine or carboxylic acid) with another group; upon exposure to light the second group cleaves from the first group, thus "deprotecting" it. In this way, you can use light to unmask the first group.

The comparatively high energy of the lowest excited states of photoactivator systems provides sufficient energy to cleave bonds. Molecules of this type are generally small conjugated systems and tend to have small two-photon cross sections. However, most molecules with large δ typically absorb at longer wavelengths, and their lowest excited states have insufficient

energy to directly cleave bonds. Therefore, we employed an alternative approach based on bond-cleavage reactions activated by electron transfer.[26] In this approach, a molecule absorbs light, creating an excited state that can transfer an electron to (or accept an electron from) a "cleavable group" (a group containing a cleavable bond) upon accepting (or giving up) an electron. When the cleavable group accepts (or donates) an electron, a bond can be broken and can lead to generation of reactive species such as radicals, acids, and bases.

In order for the electron transfer process to be efficient, the excited molecule must be sufficiently reducing or oxidizing relative to the cleavable group, and the 2PA chromophore and the photocleavable group must be in close proximity. To place the two groups in close proximity, we directly linked the electron-rich 2PA chromophore and the "cleavable group" via a covalent bond, for example, to make two-photon excitable photoacid generators.[26]

Photoacid generators are chromophores that liberate a proton or another acidic species upon excitation. Photoacid generators have been used to photoinitiate ring-opening polymerization of epoxides and to pattern polymeric materials through acid-catalyzed cleavage of active ester functional groups; for example, such reactions are the basis of many commercial patterning and lithographic processes. Epoxide systems, in particular, offer some advantages over acrylates for microfabrication by MPL, since they can be less susceptible to shrinkage and deformation. Commercially available photoacid generator systems, such as salts containing triarylsulfonium cations, are highly efficient under ultraviolet illumination, yet are far from optimized for two-photon excitation because their δ is rather small. We therefore implemented the electron transfer approach described earlier by linking a 2PA chromophore directly to a dialkylsulfonium group and activating it by two-photon excitation (Figure 4a).[26] The two-photon photoacid generator based on a bis-styrylbenzene conjugated bridge with a moderate δ was estimated to have $\delta\Phi_c \sim 400$ GM.

The photoacid in Figure 4 has been employed in a positive tone resist (i.e., a polymer system that becomes more soluble upon photoexcitation). In positive tone resins, the exposed region is removed in the development step. In one implementation, the photoacid was dissolved in an acrylate polymer system that contained acid-cleavable tetrahydropyranyl (THP) ester groups (Figure 4b), which give carboxylic acid groups upon cleavage. Exposure of the resin activated the photoacid, which after a postexposure baking process rendered the polymer soluble in aqueous base.[26,27] For structures where small voids within large volumes of solid materials are required, positive tone resists are generally preferable to negative tone resins because shorter patterning times are required. Figure 3b shows a structure comprising an array of tunnels in the polymer matrix that are connected at the ends by channels that extend to the upper surface to enable removal of the exposed and photocleaved material. We have demonstrated that the channels can be filled with various fluids, including liquid crystals, and such structures have potential for applications in microfluidics and switchable grating devices.

In addition to polymeric structures, the fabrication of structures in a variety of other materials, including metals, semiconductors, and inorganic–organic hybrids, is desirable; it is possible to pattern, by various schemes, each of these materials classes by MPL processes.[28,40,41] Stellacci et al. have demonstrated the fabrication of metallic microstructures by exposure of a nanocomposite composed of a polyvinylcarbazole/ethylcarbazole host; a soluble silver salt that can be reduced to form silver atoms; silver nanoparticles coated with a mixture of thiol ligands to promote solubility in the host and to disfavor aggregation; and a 2PA chromophore that, upon excitation, is capable of reducing the silver salt.[28] Conductive silver features were fabricated by MPL, and the fabrication of a 3D structure was demonstrated. This approach also was applied to nanocomposites based on gold and copper nanoparticles. Fourkas and co-workers have reported on an alternative surface modification approach that enables selective deposition of metal on defined regions of a polymeric structure.[30,42] Chichkov and co-workers have used acrylate functionalized trialkoxysilane-based precursors in MPL to form 3D microstructures in hybrid silica sol-gel glass material.[22,41] Dong and Perry have recently reported on the use of a titanium alkoxide complex precursor for the fabrication of titania–organic hybrid structures by MPL.[43] Another interesting development by Fourkas and co-workers, with significance for the potential mass production of 3D structures fabricated by MPL, is a soft lithography replication method based on a removable poly(dimethylsiloxane) molding process, which enables replication of structures with overhangs and even closed-loop structures.[44,45]

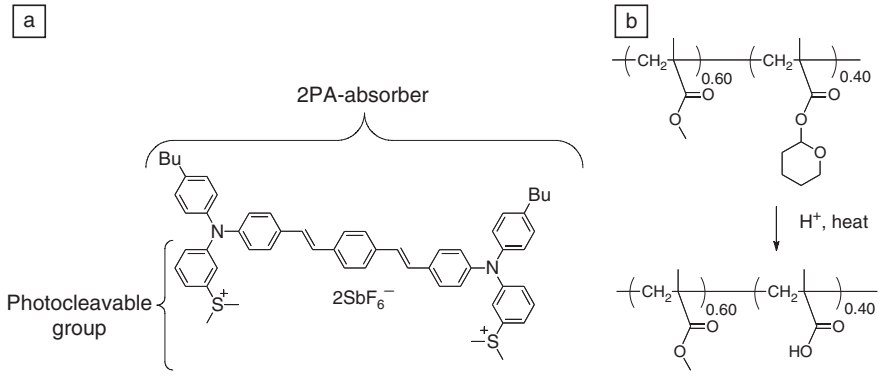

Figure 4. (a) A two-photon photoacid generator based on the linking of a two-photon-absorption chromophore and a photocleavable group. (b) Positive tone resin illustrating cleavage of acid-cleavable tetrahydropyranyl groups upon treatment with acid and postexposure bake.

Conclusions

We have highlighted the developments in photoinitiators, photoactive materials systems, and structure/device fabrication that exemplify the advances made in two-photon/multiphoton lithography. The advent of design principles for two-photon absorbing photoinitiators with large cross sections and high chemical efficiency offers a rational approach to the synthesis of optimized photoactivators with extremely high photosensitivity. Various multiphoton materials platforms have been developed, and new nanocomposites and templating approaches can provide access to a range of compositions for 3D microfabrication. Three-dimensional structures and devices fabricated with unique functionality are emerging as a result of MPL, and many possibilities remain unexplored.

Although still in its infancy, the field of MPL has advanced to the point where it is poised to have a significant impact in photonics, microelectromechanical systems, and biomedical technologies in the coming years. MPL clearly demonstrates that

two-photon absorbing molecules show significant utility for 3D processing in the solid state.

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